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Structural features of N-containing titanium dioxide thin films deposited by magnetron sputtering

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ABSTRACT

N-containing titanium dioxide (N-TiO_2) thin films have been obtained by the midrange magnetron sputtering with two-component N_2/O_2 reactive working gas. Complex analysis of the films structure and phase composition demonstrates its significant changes due to nitrogen content. X-ray diffraction data show the anatase-rutile phase transition and crystallites size reduction in N-TiO_2 thin films with increase of nitrogen content in the reactive atmosphere. The investigation has been focused on phase transition, zeta potential, chemical bonds and UV-light influence on the wettability of the films versus nitrogen concentration. Hydrophilization of N-TiO_2 films surface under UV-light has an irreversible character.

1. Introduction

Titanium dioxide (TiO_2) has attracted lots of interest the past decades due to its potential applications such as solar energy conversion [1,2], environmental purification [3], and biomaterials [4,5]. Recently, a number of studies have focused on the research of N-doped TiO_2 films prepared by a variety of physical and chemical methods [6–10]. These different synthetic procedures lead to forming the N-doped TiO_2 films with different properties. The main idea of these works is narrowing of TiO_2 band gap by nitrogen substitution.

The nitrogen atoms location in TiO_2 lattice (substitutional or interstitial) is studied using several techniques for instance X-ray photoelectron spectroscopy, X-ray absorption spectroscopy, in particular, extended X-ray absorption fine structure, electron paramagnetic resonance spectroscopy etc. [11–16]. However, the exact location of the nitrogen anion in the titanium dioxide films remains uncertain, because the films structure created by magnetron sputtering depends on deposition mode and might consist of crystallites separated by amorphous regions [17].

The films fabricated by ion-plasma methods have a number of advantages. They are homogeneous, dense, and transparent, possess good mechanical characteristics, do not contain visible defects such as cracks and discontinuities [18,19]. Ion-plasma methods allow controlling impurity concentration and level of film crystallinity. This is the main reason to believe in the prospects of their use.

A lot of works are directed on the improving of photocatalytic and self-cleaning features of TiO_2 films [20–22]. For this purpose, the crystalline structure of the films is of great significance. Anatase is known as an effective material for photocatalysis and, furthermore, there is concept that anatase-rutile biphasic system can be promising for heterogeneous photocatalysis. This is attributed to the defects at the anatase-rutile separation boundary that increase the photocatalytic activity of the mixture [23]. According to paper [24] the nitrogen presence inhibits the TiO_2 rutile phase growth and stimulates the transition from rutile to anatase in the film, while the nitrogen content in plasma discharge increases.

The biocompatibility improvement of implants interacting with organism is a present-day trend in biomedical materials science. Since the rutile phase is more chemically stable than the anatase in biological liquids and the release of metallic ions from implant into surrounding can be decreased by TiO_2 coating formation [25]. The use of the rutile thin film as a surface layer on the implants can improve the biocompatibility [26,27].

Surface wettability is an important factor describing the materials interaction with liquids, proteins and cells adhesion. The hydrophobic surfaces (low energy) are prone to absorb more proteins, while the hydrophilic surfaces (high energy) are prone to prevent protein adsorption and suppress platelet adhesion and blood clot formation. However, highly hydrophobic surfaces can reduce protein and platelet adsorption as well [28]. Hydrophobicity or hydrophilicity of the surface is associated with the surface energy, which is a consequence of the

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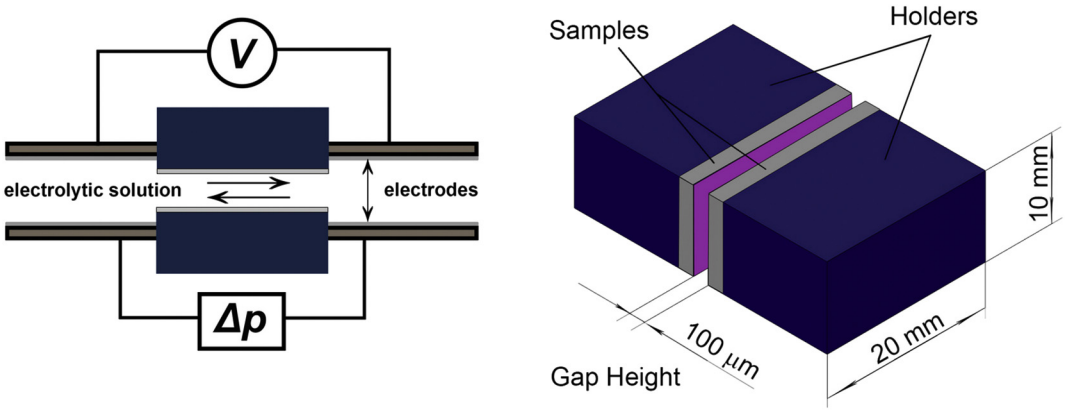

Fig. 1. The schematic diagram of the measurement cell and cell holders.

charge distribution depending on the surface chemistry and its properties [28].

Zeta (ζ-) potential is an essential parameter while describing the ion adsorption and electrostatic surface-environment interactions. Zeta potential knowledge of surfaces is of interest when developing biomaterials. ζ-potential changes can have influence on the protein adsorption acceleration and cell growth [29].

It was found previously [8,30,31] that it is possible to use the midrange magnetron reactive sputtering (MRS) deposition process with different nitrogen content in the plasma to control the phase composition of growing TiO_2 films. Therefore, the aim of this study is to evaluate the potential of MRS technique to obtain the TiO_2 films with determined phase composition and nitrogen content. This work presents study of the crystalline structure and its features concerned with nitrogen incorporation during TiO_2 films growth in abnormal magnetron plasma discharge. The investigation has been focused on phase transition, zeta potential, chemical bonds and UV-light influence on the wettability of N-TiO_2 films versus nitrogen concentration.

2. Materials and methods

N-containing titanium dioxide (N-TiO_2) thin films have been deposited onto stainless steel (12Cr18Ni10Ti) due to its application as a material for coronary stents production [32,33] and silicon wafers used for SEM cross-sectional analysis by means of a handmade reactive magnetron sputtering system (Tomsk Polytechnic University, Tomsk). A commercially pure titanium target (cathode) was sputtered in a reactive atmosphere composed of oxygen and nitrogen in different flow ratio ($p(N_2)/p(O_2) = 1$ and 3). Deposition was carried out at total pressure of 0.1 Pa, the power of 1 kW and current of 3 A in O_2 and N_2/O_2 mixture atmospheres. The distance between the substrate and the target was 100 mm. Flow rates were controlled by monitoring of optical emission spectra (AvaSpec-3648 spectrometer) and by probe method using conditions shown to deposit N-TiO_2 films [31,34]. The substrate temperature was 130°C during the deposition process.

The N-TiO_2 films morphology was observed with scanning electron microscope (SEM) ESEM Quanta 400 (FEG, FEI) with EDX-analyzer (EDS, Genesis 4000, S-UTW-Si(Li) detector). The phase composition and crystalline structure of N-TiO_2 films were identified by X-ray diffraction. Diffractometer (XRD-7000, Shimadzu) with glancing angle geometry was used; an incidence angle was of 1°. Measurements were carried out at 30 kV, 30 mA with a Cu-Kα radiation ($\lambda = 0.15418$ nm), a sampling pitch of 0.03° in the 2θ range of 10–70°. Phase volume ratio and mean crystallite size were calculated by PowderCell 2.4 software using Rietveld method and Scherrer formula [35]. PDF-4 database of International Center for Diffraction Data (ICDD) was used for the phase analysis of the thin films.

Raman spectra were obtained by the setup developed in the Fraunhofer IKTS-MD using of a microscopic reflection system, consisting of invert microscope (ZEISS, Axiovert), spectrometer (iHR550) with TE-cooled CCD (thermoelectrically cooled charge-coupled device) and detector (both of Horiba, JobinYvon Inc.). Diode-pumped solid crystal laser with excitation wavelength 632.8 nm was used. The spot diameter on the sample was below 5 μm. The total excitation power varied in the range of 0.3–1.5 mW. Scattered light was collected by a 100× ZEISS LD EC Epiplan objective. The exposure time for single point measurement was 20s, 35 accumulations per point measurement were performed. The region of spectrum scattering detection was from 100 to 900 cm^{-1}. All spectra deconvolution was using the Gaussian function.

Fourier transform infrared (FT-IR) spectra were used for identification of the chemical bonds in the thin films. All samples were scanned within the wave range of 400–2500 cm^{-1} using a Thermo Nicolet 5700 spectrometer. The optical spectrum lines were determined by using National Institute of Standards and Technology Databases (NIST) [36]. The films thickness was measured with optical spectrometer (AvaSpec-2048-USB2) and was of the order (250 ÷ 500) nm.

X-ray photoelectron spectroscopy (XPS) was performed on a K-Alpha + spectrometer (Thermo Fisher Scientific) using a microfocused, monochromated Al Kα X-ray source (30–400 μm spot size). The K-Alpha charge compensation system was employed during analysis, using electrons of 8 eV energy and low-energy argon ions to prevent any localized charge build-up. Data acquisition and processing using the Thermo Avantage software is described elsewhere [37]. The spectra were fitted with one or more Voigt profiles (BE uncertainty: ±0.2 eV). The analyzer transmission function, Scofield sensitivity factors [38], and effective attenuation lengths (EALs) for photoelectrons were

Table 1
Samples groups and their characteristics depending on N_2/O_2 mass flow ratio.

Samples	N_2/O_2 mass flow ratio	Elemental composition according to EDX data			Phase volume ratio (%)		Mean crystallite size (nm)	
		Ti, at%	O, at%	N, at%	Anatase	Rutile	Anatase	Rutile
TiO_2 (#I)	0	15.59	84.40	–	70	23	20	12
N-TiO_2 (#II)	1	14.27	70.67	15.06	14	70	14	12
N-TiO_2 (#III)	3	17.78	65.13	17.09	13	72	13	12